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**Water Soluble, Conjugated Main Chain Azo
Polymer: Synthesis and Characterization**

by

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**Water Soluble, Conjugated Main Chain Azo polymer:
Synthesis and Characterization**

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Summary

The monomer 2,5-diaminobenzene sulfonic acid has been polymerized to a high molecular weight, conjugated main chain azo polymer. The presence of the azo group in the polymer was confirmed using Raman spectroscopy. The polymer is highly soluble in water over a wide pH range. It is also soluble in common polar organic solvents such as DMF, DMSO, and NMP.

Introduction

Polymers containing the azo (-N=N-) group have been extensively investigated for application in the field of optoelectronics¹⁻³⁾. Photoinduced trans-cis-trans isomerization of azo chromophores has been utilized in optical information storage⁴⁻⁶⁾. Formation of surface relief gratings in amorphous polymers⁴⁾, phase transitions in liquid crystalline polymers⁵⁾, and photoinduced optical birefringence⁶⁾ through photoinduced reorientation of the azo chromophore have been reported in the literature. Application of donor-acceptor substituted azo compounds as nonlinear optical chromophores have been explored in great detail^{7,8)}.

Most of these polymers are side chain azo polymers or polymers containing isolated azo groups in the main chain⁹⁾. Reports of conjugated, main chain azo polymers are relatively rare. Widespread applications of conjugated polymers such as polyanilines¹⁰⁾, polyphenylene vinylenes¹¹⁾, and polythiophenes¹²⁾ as conducting polymers and luminescent materials, among others, have motivated research in the direction of conjugated azo polymers. Conjugated main chain azo polymers are expected to exhibit interesting optical and electronic properties.

Attempts to synthesize conjugated azo polymers have usually resulted in intractable and insoluble polymers. Polycondensation¹³⁾ and Wittig reaction¹⁴⁾ are some of the few methods reported for the synthesis of main chain conjugated azo polymers. However the molecular weight of such polymers are often low and these polymers have poor solubility. Catalyzed oxidative coupling of aromatic amines have been reported to yield azo derivatives¹⁵⁾. Primary aromatic amines such as aniline can be converted to azobenzenes by Cu⁺ catalyzed oxidation with oxygen and pyridine. This method has been utilized to synthesize azo polymers from aromatic diamines¹⁶⁾ (Scheme 1).

In this approach also the molecular weights of the final products are usually low. This is attributed to the poor solubility of the product. The intractable and

insoluble nature of these polymers makes characterization and post processing extremely difficult. The oxidative coupling of aromatic diamines can also result in side reactions leading to the formation of polyaniline type products due to the oxidation of the aromatic ring¹⁷⁾.

In this paper we report the polymerization of 2,5-diaminobenzene sulfonic acid to yield a high molecular weight, conjugated, azo polymer through the sodium perborate/boric acid oxidative coupling route¹⁸⁾ (Scheme 2). This monomer and the approach were selected for two reasons. First, increasing the oxidation potential of the monomer reduces the possibility of oxidation of the aromatic ring, significantly reducing the possibility of side reactions. Secondly, the sulfonic acid group increases the possibility of solubilization of the resultant polymer. The polymer may be further processed into mono and multilayer assemblies¹⁹⁾. Sulfonated polyanilines for example, have been fabricated into multilayer heterostructure light emitting diode devices²⁰⁾.

Experimental part

Materials

The monomer 2,5-diaminobenzene sulfonic acid was obtained from Aldrich and recrystallized from water. The reagents sodium perborate tetrahydrate and boric acid were also obtained from Aldrich and used without further purification. Reagent grade THF, methanol and ethanol were obtained from VWR Scientific and used without further purification.

Oxidative coupling of 2,5-diaminobenzene sulfonic acid (DABSA) was carried out in water in the presence of sodium perborate and boric acid at 70° C for 6 hours. The recrystallized monomer DABSA (2,0 g, 10,6 mmol), sodium perborate tetrahydrate (4,4 g, 28,5 mmol), and boric acid (1,1 g, 17,9 mmol) were taken in an RB flask and 70 mL of water was added. The mixture was heated to 70° C for 6

hours. The solution turned deep red within a few minutes after the start of the reaction. After 6 hours 0,5 g of sodium perborate and 0,1 g of boric acid were added and the reaction was continued for another 6 hours. The process was repeated one more time and then the red solution was concentrated and the polymer (PDABSA) was precipitated by pouring the solution into THF. The reddish brown powder obtained was filtered and dried in a vacuum oven. The yield of the polymer was 1,8 g. The resulting polymer is soluble in water, methanol, and other highly polar organic solvents such as dimethyl formamide, dimethyl sulfoxide, and N-methyl pyrrolidone.

$(C_6H_4N_2O_3S)_n$	Calc.	C 39,13	H 2,19	N 15,21	O 26,05	S 17,42
	Found	C 39,09	H 2,87	N 15,04	O 26,12	S 16,88

Characterization

The infrared spectrum was recorded with Perkin-Elmer 1760X FTIR spectrometer and the Raman scattering spectrum was obtained using Perkin-Elmer 1700X FTRaman spectrometer. The UV-Vis spectra were recorded using a Perkin-Elmer Lambda-9 UV/VIS/NIR spectrophotometer. The molecular weight was determined using Gel Permeation Chromatography instrument Waters Model 510 pump, Waters Model 410 refractive index detector with styragel columns relative to polystyrene standards. The GPC analysis was carried out with DMF containing 1 mol% LiBr as the eluent. Addition of more than 0.5 mol% salt in the eluent yields acceptable molecular weight results in the case of polyelectrolytes^{21).}

Results and Discussion

A water soluble, main-chain conjugated azo polymer was successfully synthesized. GPC analysis of the polymer with DMF containing 1 mol% LiBr as eluent indicates that the polymer has a number average molecular weight of 7,100 and a

weight average molecular weight of 12,500. This is the first report of a high molecular weight, conjugated, water soluble main chain azo polymer. The PDABSA is soluble over a wide range of pH.

The polymer structure is characterized using FTIR, and FTRaman spectroscopy. The FTIR and FTRaman spectra of the polymer are shown in Figures 1 and 2 respectively .

During the polymerization, the amino groups undergo oxidative coupling to the azo group. The formation of azo group was confirmed using Raman spectroscopy. Due to the nonpolar nature of the -N=N- group, no corresponding peak appears in the infrared spectrum. The peak at 1532 cm^{-1} in the Raman spectrum is due to the symmetric stretch of the azo group. A broad peak appears in the infrared spectrum at around 3400 cm^{-1} . This may be due to the formation of some polyaniline type segments in the polymer structure (Figure 3). Due to the presence of free amino and sulfonic acid groups some zwitter-ionic structures at low pH values may be expected.

It may not be possible to completely avoid such side reactions. The complexity of the aromatic region of the ^1H NMR spectrum also indicates that there is a possibility of some polyaniline type structure. The UV-vis spectrum of the aqueous solutions of the monomer and the polymer are shown in Figure 4.

In conclusion we have synthesized a high molecular weight, conjugated main chain azo polymer. The formation of azo polymer was confirmed using Raman spectroscopy. The polymer is highly soluble in water over a wide range of pH. It is also soluble in polar organic solvents such as DMF, DMSO, and NMP. The fluorescence behavior and multilayer fabrication will be reported in a subsequent publication.

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References

1. H. Katz, K. Singer, J. Sohn, C. Dirk, L. King, H. Gordon, *J. Am. Chem. Soc.* **109**, 6561 (1987).
2. C. Xu, B. Wu, L. R. Dalton, P. M. Ramon, Y. Shi, W. H. Steier, *Macromolecules* **25**, 6716 (1992).
3. M. A. Hubbard, T. J. Marks, W. Lin, G. K. Wong, *Chem. Mater.* **4**, 965 (1992).
4. D. Y. Kim, L. Li, X. L. Jiang, V. Shivshankar, J. Kumar, S. K. Tripathy, *Macromolecules* **28**, 8835 (1995).
5. M. Eich, J. H. Wendorff, B. Reck, H. Ringsdorf, *Makromol. Chem., Rapid Commun.* **8**, 59 (1987).
6. T. Todorov, L. Nikolova, N. Tomova, *Appl. Opt.* **23**, 4309 (1984).
7. R. J. Jeng, Y. M. Chen, A. K. Jain, J. Kumar, S. K. Tripathy, *Chem. Mater.* **4**, 1141 (1992).
8. L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steier, M. Ziari, H. Fetterman, Y. Shi, R. V. Mustacich, A. K.-Y. Jen, K. J. Shea, *Chem. Mater.* **7**, 1060 (1995).
9. H. K. Hall, Jr., T. Kuo, R. W. Lenz, T. M. Leslie, *Macromolecules* **20**, 2041 (1987).
10. W. S. Huang, B. D. Humphrey, A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1* **82**, 2385 (1986).
11. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **347**, 539 (1990).
12. D. Braun, G. Gustafsson, D. McBranch, A. J. Heeger, *J. Appl. Phys.* **72**, 564 (1992).
13. G. Kossmehl, J. Wallis, *Makromol. Chem.* **183**, 347 (1982).
14. G. Kossmehl, J. Wallis, *Makromol. Chem.* **183**, 331 (1982).
15. A. P. Terent'ev, Ya. D. Mogilyanskii, *Dokl. Akad. Nauk SSSR* **103**, 91 (1955).

16. H. C. Bach, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **7**, 576 (1966).
17. A. H. Premasiri, W. B. Euler, *Macromol. Chem. Phys.*, **196**, 3655 (1995).
18. P. Santurri, F. Robbins, R. Stubbings, *Organic Syntheses*, **V**, 341 (1973).
19. S. Balasubramanian, J. Kumar, S. K. Tripathy, manuscript in preparation.
20. M. Ferreira, M. F. Rubner, *Macromolecules* **28**, 7107 (1995).
21. A. Domard, M. Rinaudo, C. Rochas, *J. Polym. Sci. Polym. Phys. Ed.* **17**, 673 (1979).

Scheme 1. Catalyzed oxidative coupling of amines to azo derivatives.

Scheme 2. Polymerization of 2,5-diaminobenzene sulfonic acid by perborate/boric acid oxidative coupling reaction.

Figure 1. FTIR spectrum of poly(azo-3-hydroxysulfonyl-1,4-phenylene)

Figure 2. FTRaman spectrum of poly(azo-3-hydroxysulfonyl-1,4-phenylene)

Figure 3. Possible polyaniline type structure formation during oxidative coupling of 2,5-diaminobenzene sulfonic acid.

Figure 4. UV-Vis spectrum of aqueous solutions of a) 2,5-diaminobenzene sulfonic acid and b) poly(azo-3-hydroxysulfonyl-1,4-phenylene).











